

Crystal Structures and Luminescent Properties of Three Coordination Polymers Based on 2,5-Furandicarboxylic Acid Ligand and 1,10-Phenanthroline

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ABSTRACT Three new coordination polymers, namely $[Zn(FDA)(phen)(H_2O)_2]_n$ (**1**), $[Cd(HFDA)(phen)_2(NO_3)]_n$ (**2**) and $[Cd(FDA)(phen)]_n$ (**3**) ($H_2FDA = 2,5$ -furandicarboxylic acid, phen = 1,10-phenanthroline) have been synthesized by the solvothermal method and characterized by elemental analysis, IR, powder X-ray diffraction, thermogravimetric analysis and X-ray single-crystal diffraction analysis. For **1**, the neighboring Zn^{2+} ions are bridged by FDA^{2-} as linkers to form one-dimensional (1D) chains, and phen ligands are as the terminal ligands. Furthermore, the 1D chains are packed into a three-dimensional (3D) supramolecular structure through hydrogen bonds and $\pi-\pi$ interactions. For **2**, the H_2FDA ligand is partial deprotonation, which is a rare phenomenon among other coordination polymers based on H_2FDA . Under the synergetic effect of phen ligands and the partial deprotonation of H_2FDA , the structure of **2** is discrete. For **3**, the Cd^{2+} ions are linked by two carboxylates of FDA^{2-} ligand to give rise to 1D zig-zag chains, and phen ligands chelate the Cd^{2+} ions like **1**. In addition, solid-state luminescent spectra of three coordination polymers were also studied at room temperature.

Keywords: 2,5-furandicarboxylic acid; 1,10-phenanthroline; crystal structure;

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1 INTRODUCTION

Coordination polymers (CPs) with their fascinating topological structures assembled from metal ions and organic ligands have attracted much attention mainly due to their potential applications in the fields of

selective adsorption and separation^[1], catalysis^[2], molecular magnetism^[3], fluorescence^[4] and so on. It is generally known that organic ligands play a crucial role in the structural assembly of CPs because the length, angle, rigidity, coordination mode and coordination capacity, functional groups or substituents of the organic ligands have important impacts during the process of self-assembly^[5]. Therefore, the choice of appropriate organic ligand can help us to build the required frameworks.

Up to now, multidentate carboxylic acid ligands have been widely used in the synthesis of CPs^[6]. Among numerous multidentate carboxylic acid ligands, 2,5-furandicarboxylic acid (H₂FDA) is a typical multidentate carboxylate ligand^[7]. A number of 2,5-furandicarboxylic acid-based CPs have been reported, due to its strong coordination ability as a multifunctional "V" type dicarboxylic acid ligand^[8]. To further enrich the coordination chemistry of 2,5-furandicarboxylic acid and to develop new functional CPs, we introduced a typical chelating N,N'-based secondary ligand, 1,10-phenanthroline (phen), because of its excellent coordination ability and large conjugated system. In this work, we used 2,5-furandicarboxylic acid as the main organic building block and 1,10-phenanthroline (phen) as the secondary ligand to construct three new CPs. Furthermore, the luminescent properties of three complexes have also been investigated.

2 EXPERIMENTAL

2.1 General procedures

All of the solvents and reagents for synthesis were commercially available and used as received. Elemental analyses (C, H and N) were performed on a Perkin-Elemer240C analyzer. IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Thermogravimetric (TG) analyses were carried out on a Rigaku standard TG-DTA analyzer at a heating rate of 10 °C min⁻¹ from ambient temperature to 700 °C, and an empty Al₂O₃ crucible was used as reference. The powder X-ray diffraction (PXRD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the PXRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 1.4.2 available free of charge via the Internet at <http://www.iucr.org>. Luminescence spectra were investigated on an Edinburgh FS5 spectrophotometer.

2.2 Synthesis

[Zn(FDA)(phen)(H₂O)_n] (1) Zn(NO₃)₂ 6H₂O (0.0297 g, 0.1 mmol), H₂FDA (0.0156 g, 0.1 mmol) and phen (0.0180 g, 0.1 mmol) were mixed with DMAC:H₂O (V:V = 1:1, 5 mL) in a 25 mL Teflon

liner under hydrothermal conditions at 120 °C for three days, and then cooled to room temperature at a rate of 4 °C·h⁻¹. The colorless crystals were obtained (yield: 20% based on Zn). FT-IR (KBr pellets, cm⁻¹): 3261 m, 1629 s, 1608 s, 1576 s, 1517 m, 1495 w, 1428 m, 1358 s, 1336 s, 1222 w, 1161 w, 1031 w, 965 w, 869 w, 855 m, 815 w, 785 m, 727 m, 644 w, 552 w, 491 w. Anal. Calcd. for C₁₈H₁₄ZnN₂O₇: C, 49.62; H, 3.24; N, 6.43%. Found: C, 49.55; H, 3.26; N, 6.39%.

[Cd(HFDA)(phen)₂(NO₃)] (**2**) Cd(NO₃)₂ 4H₂O (0.0308 g, 0.1 mmol), H₂FDA (0.0156 g, 0.1 mmol) and phen (0.0180 g, 0.1 mmol) were mixed with water (10 ml) in a 25 mL Teflon liner under hydrothermal conditions at 120 °C for three days, and then cooled to room temperature at a rate of 4 °C·h⁻¹. The colorless crystals were obtained (yield: 35% based on Cd). FT-IR (KBr pellets, cm⁻¹): 3435 s, 1724 m, 1651 w, 1594 s, 1574 m, 1557 w, 1515 m, 1427 m, 1384 s, 1368 s, 1346 s, 1266 m, 1214 w, 1145 w, 1101 w, 844 m, 815 w, 790 w, 728 s, 637 w. Anal. Calcd. for C₃₀H₁₈CdN₅O₈: C, 52.23; H, 2.77; N, 10.15%. Found: C, 52.38; H, 2.60; N, 10.13%.

[Cd(FDA)(phen)]_n (**3**) This complex was synthesized by a procedure similar to that of **2**, except that water was used instead of ethanol. The colorless crystals were obtained (yield: 35% based on Cd). FT-IR (KBr pellets, cm⁻¹): 3431 m, 3115 m, 1568 s, 1517 s, 1434 m, 1418 m, 1376 s, 1222 w, 1140 w, 1102 w, 1039 w, 964 m, 857 w, 821 s, 795 m, 728 s, 642 w, 574 w, 507 w. Calcd. for C₁₈H₁₀CdN₂O₅: C, 48.40; H, 2.26; N, 6.27%. Found: C, 48.36; H, 2.23; N, 6.23%.

2.3 Crystal structure determination and refinement

Single-crystal X-ray diffraction data were collected on a Bruker-AXS SMART APEX2 CCD diffractometer at 296(2) K with a Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The program SAINTPLUS was used for integration of the diffraction profiles^[9]. All the structures were solved by direct methods using the SHELXS program and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied using the SADABS program)^[10]. Metal atoms in each complex were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on *F*². The hydrogen atoms of ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The crystallographic data are listed in Table 1. The selected bond lengths and bond angles for **1**~**3** are given in Table 2. Hydrogen bonds for **1**~**3** are listed in Table 3.

Table 1. Crystal Data and Structure Refinement Parameters for Complexes **1**~**3**

	1	2	3
Empirical formula	C ₁₈ H ₁₄ ZnN ₂ O ₇	C ₃₀ H ₁₉ CdN ₅ O ₈	C ₁₈ H ₁₀ CdN ₂ O ₅
Formula weight	435.68	689.90	446.68
Temperature/K	296(2)	296(2)	296(2)
Crystal system	Triclinic	Monoclinic	monoclinic
Space group	P ₁	Cc	P2 ₁ /n
<i>a</i> / Å	8.2834(12)	11.241(3)	5.824(5)
<i>b</i> / Å	9.3099(14)	18.460(4)	15.907(12)
<i>c</i> / Å	13.0084(19)	13.413(5)	18.712(15)
α / °	70.767(4)	90	90
β / °	87.727(4)	101.131(4)	92.535(12)
γ / °	66.958(4)	90	90
<i>V</i> (Å ³)	867.0(2)	2731.0(14)	1732(2)
<i>Z</i>	2	4	4
<i>D_c</i> (g cm ⁻³)	1.669	1.678	1.713
<i>F</i> (000)	444	1384	880
θ range / °	2.50~25.00	2.40~24.80	2.50~24.90
Reflns. collected	5465	8357	7719
Independent reflns.	3001	3744	3039
Goodness-of-fit	1.020	1.030	1.070
<i>R</i> ^a (<i>I</i> > 2σ(<i>I</i>))	0.063	0.036	0.148
<i>wR</i> ^b (<i>I</i> > 2σ(<i>I</i>))	0.182	0.097	0.341
(Δρ) _{max} , (Δρ) _{min} / e·Å ⁻³	1.45, -0.73	1.63, -0.38	3.49, -3.42

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for Complexes 1~3

1			
Bond	Dist.	Bond	Dist.
Zn(1)–O(4i)	2.011(5)	Zn(1)–N(2)	2.107(6)
Zn(1)–O(2)	2.018(5)	Zn(1)–N(1)	2.134(7)
Zn(1)–O(1W)	2.099(6)		
Angle	(°)	Angle	(°)
O(4i)–Zn(1)–O(2)	128.7(2)	O(1W)–Zn(1)–N(2)	91.7(2)
O(4i)–Zn(1)–O(1W)	89.6(2)	O(4i)–Zn(1)–N(1)	95.5(2)
O(2)–Zn(1)–O(1W)	91.5(2)	O(2)–Zn(1)–N(1)	92.3(2)
O(4i)–Zn(1)–N(2)	99.5(2)	O(1W)–Zn(1)–N(1)	169.6(2)
O(2)–Zn(1)–N(2)	131.6(2)	N(2)–Zn(1)–N(1)	78.5(2)
2			
Bond	Dist.	Bond	Dist.
Cd(1)–N(2)	2.363(7)	Cd(1)–N(3)	2.418(7)
Cd(1)–O(7)	2.370(8)	Cd(1)–N(1)	2.461(9)
Cd(1)–N(4)	2.373(9)	Cd(1)–O(2)	2.547(6)
Cd(1)–O(1)	2.375(6)		
Angle	(°)	Angle	(°)
N(2)–Cd(1)–N(4)	92.7(3)	O(7)–Cd(1)–N(3)	87.0(3)
O(7)–Cd(1)–N(4)	77.2(3)	N(4)–Cd(1)–N(3)	68.7(3)
N(2)–Cd(1)–O(1)	94.2(3)	O(1)–Cd(1)–N(3)	160.5(2)
O(7)–Cd(1)–O(1)	89.40(18)	N(2)–Cd(1)–N(1)	70.7(2)
N(4)–Cd(1)–O(1)	128.9(2)	O(7)–Cd(1)–N(1)	120.0(2)
N(4)–Cd(1)–N(1)	150.06(15)	O(7)–Cd(1)–O(2)	90.4(2)

O(1)–Cd(1)–N(1)	78.4(2)	N(4)–Cd(1)–O(2)	77.9(2)
N(3)–Cd(1)–N(1)	86.9(3)	O(1)–Cd(1)–O(2)	52.9(2)
N(2)–Cd(1)–O(2)	83.7(2)	N(3)–Cd(1)–O(2)	146.2(2)
N(1)–Cd(1)–O(2)	122.8(2)		
3			
Bond	Dist.	Bond	Dist.
Cd(1)–O(4)	2.338(16)	Cd(1)–O(1)	2.342(15)
Cd(1)–N(2)	2.314(17)	Cd(1)–O(3)	2.353(12)
Cd(1)–N(1)	2.32(2)	Cd(1)–O(2)	2.387(11)
Angle	(°)	Angle	(°)
O(4)–Cd(1)–N(1)	105.7(6)	N(2)–Cd(1)–O(3)	145.7(5)
N(2)–Cd(1)–N(1)	73.7(6)	N(1)–Cd(1)–O(3)	98.1(6)
O(4)–Cd(1)–O(1)	147.6(6)	O(1)–Cd(1)–O(3)	101.1(5)
N(2)–Cd(1)–O(1)	113.0(6)	O(4)–Cd(1)–O(2)	104.1(5)
N(1)–Cd(1)–O(1)	99.4(6)	N(2)–Cd(1)–O(2)	95.9(6)
N(1)–Cd(1)–O(2)	148.9(6)	O(3)–Cd(1)–O(2)	105.8(5)
O(1)–Cd(1)–O(2)	57.1(4)		

Symmetry transformation: (i) $x+1, y-1, z$ for **1**

Table 3. Hydrogen Bond Lengths (Å) and Bond Angles (°) of Complexes 1~2

D–H···A	d(D–H)	d(H···A)	d(D···A)	<DHA
1				
O(1w)–H(1wa)···O(2i)	0.84(7)	1.90(8)	2.710(7)	161(9)
O(1w)–H(1wb)···O(5ii)	0.85(11)	1.91(12)	2.692(9)	153(12)
O(2w)–H(2wa)···O(1)	0.83(14)	2.55(12)	3.350(14)	164(-1)
O(2w)–H(2wb)···O(4)	0.9(2)	2.5(3)	3.012(13)	125(-1)
2				
O(5)–H(1)···O(9)(iii)	0.84(7)	1.91(7)	2.694(9)	156(8)

Symmetry transformation: (i) $1-x, -y, 1-z$; (ii) $-x, 1-y, 1-z$ for **1**, (iii) $-1+x, 1-y, -0.5+z$ for **2**

3 RESULTS AND DISCUSSION

3.1 Crystal structure of [Zn(FDA)(phen)(H₂O)₂]_n (**1**)

Single-crystal X-ray diffraction analysis shows that complex **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit of **1** consists of one Zn²⁺ ion, one FDA²⁻ ligand, one phen ligand, one coordinated water molecule and one lattice water molecule. The Zn²⁺ center is five-coordinated with two carboxylate oxygen atoms from two individual FDA²⁻, one oxygen atom from coordinated water molecule and two nitrogen atoms from a phen ligand, forming trigonal bipyramidal geometry (Fig. 1a). The distances of

$\text{Zn(II)}-\text{O}$ and $\text{Zn(II)}-\text{N}$ are in the ranges of $2.012(5)\sim2.099$ (6) and $2.107(6)\sim2.135$ (6) Å, respectively. The FDA^{2-} ligand shows a $\mu_2\text{-}(\eta^1)\text{-}(\eta^1)$ coordination mode to connect two Zn^{2+} ions. Neighboring Zn^{2+} ions are bridged by FDA^{2-} as linkers to form one-dimensional (1D) chains, and phen ligands are as the terminal ligands (Fig. 1b). The neighboring phen ligands are stacked with each other, and the centroid-centroid distances are about $3.643(5)$ and $3.569(6)$ Å, indicating significant $\pi\text{-}\pi$ interaction. In addition, the intermolecular $\pi\text{-}\pi$ interaction between the furan of H_2FDA ligands with the centroid-centroid distances of $3.650(3)$ Å links the adjacent 1D chains. Furthermore, the 1D chains are packed into a three-dimensional (3D) supramolecular structure through hydrogen bonds ($\text{O}-\text{H}\cdots\text{O}$) and $\pi\text{-}\pi$ interactions (Fig. 1c).

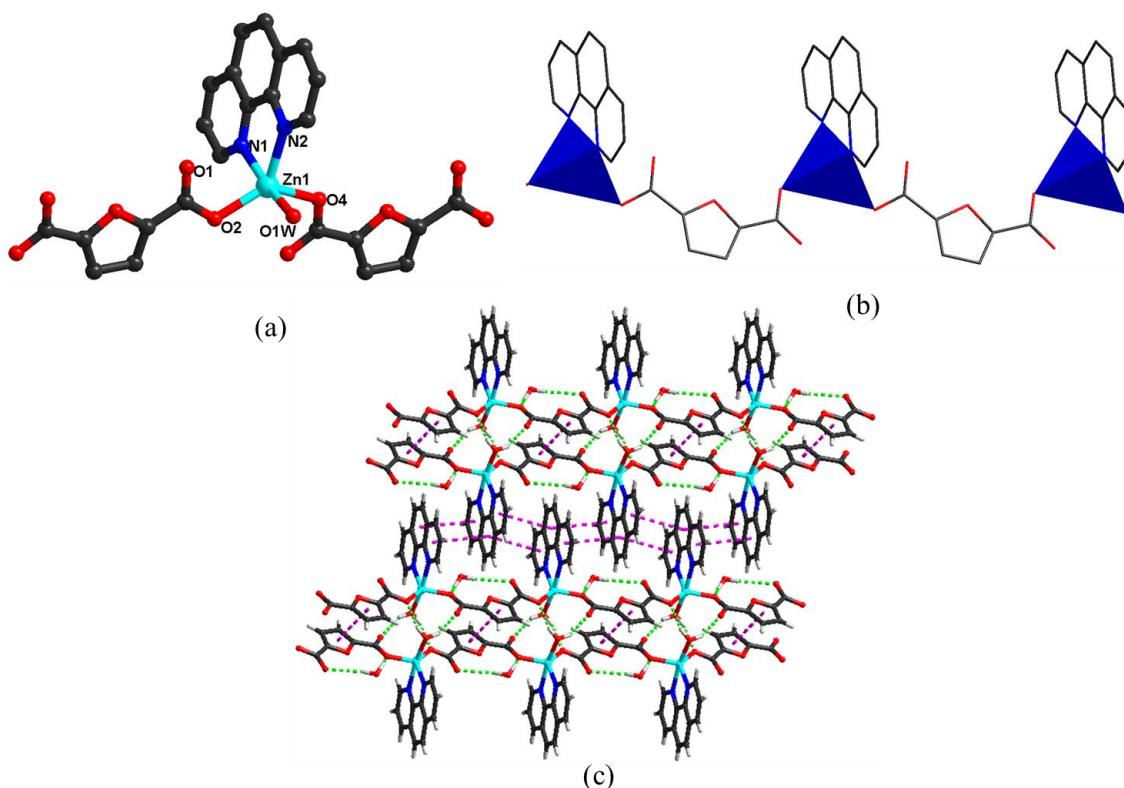


Fig. 1. (a) Asymmetric unit of **1**. (b) 1D chain in **1**. (c) 3D supramolecular structure of **1**
(Green dashed lines for hydrogen bonds, and purple dashed lines for the $\pi\text{-}\pi$ interaction)

3.2 Crystal structure of $[\text{Cd}(\text{HFDA})(\text{phen})_2(\text{NO}_3)]$ (2)

Single-crystal X-ray diffraction analysis reveals that complex **2** crystallizes in the monoclinic space group *Cc* with the asymmetric unit containing one Cd^{2+} ion, one HFDA^- ligand, two phen ligands and one NO_3^- . As shown in Fig. 2a, the center of Cd(II) is seven-coordinated by two carboxylate oxygen atoms from one individual FDA^{2-} ligand, one oxygen atom from one NO_3^- and four nitrogen atoms from two phen ligands, forming a pentagonal bipyramidal geometry. The distances of $\text{Cd(II)}-\text{O}$ and $\text{Cd(II)}-\text{N}$ locate in the ranges of

$2.371(8)\sim2.547(6)$ and $2.362(7)\sim2.464(9)$ Å, respectively. In **2**, the H₂FDA ligand is partially deprotonated, which is a rare phenomenon among other coordination polymers based on H₂FDA^[11]. Under the synergetic effect of phen ligands and the partial deprotonation of H₂FDA, the structure of **2** is discrete. The hydrogen atom from COOH with the oxygen atom from NO₃⁻ form the hydrogen bond which connects adjacent discrete units to construct 1D zig-zag chains (Fig. 2b). In addition, the intermolecular $\pi\text{-}\pi$ interaction between the furan of H₂FDA ligand and the benzene of phen ligand with the centroid-centroid distance of 3.767(7) Å links the adjacent discrete units. Moreover, 1D chains are packed into a 3D supramolecular structure through hydrogen bonds (O–H \cdots O and $\pi\text{-}\pi$ interactions) (Fig. 2c).

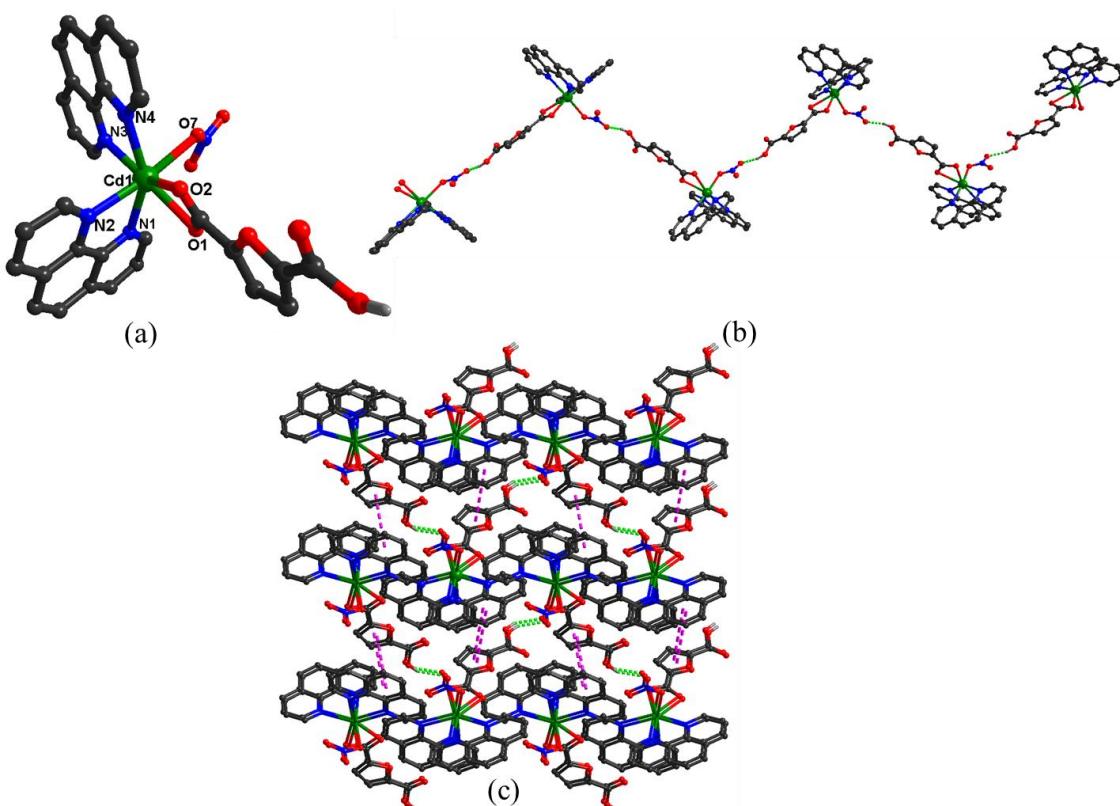


Fig. 2. (a) Asymmetric unit of **2**. (b) 1D zig-zag chain in **2**. (c) 3D supramolecular structure of **2** (green dashed lines for hydrogen bonds, and purple dashed lines for $\pi\text{-}\pi$ interaction)

3.3 Crystal structure of [Cd(FDA)(phen)]_n (**3**)

Single-crystal X-ray diffraction analysis shows that complex **3** crystallizes in monoclinic, space group $P2_1/n$ with the asymmetric unit consisting of one Cd²⁺ ion, one FDA²⁻ ligand and one phen ligand. The Zn²⁺ ion is coordinated by four oxygen atoms from two carboxyl groups of two different FDA²⁻ ligands and two nitrogen atoms from one phen ligand, exhibiting distorted octahedral coordination (Fig. 3a). The distances of Cd(II)–O and Cd(II)–N fall in the ranges of $2.338(16)\sim2.387(11)$ and $2.314(17)\sim2.32(2)$ Å, respectively.

The FDA²⁻ ligand shows a μ_2 -(η^1,η^1)-(η^1,η^1) coordination mode to connect two Cd²⁺ ions. The Cd²⁺ ions are linked by two carboxylates of FDA²⁻ ligand to give rise to infinite zig-zag chains, and phen ligands chelate Cd²⁺ for preventing the extending of the 1D chain (Fig. 3b). However, phen ligands provide abundant donors of hydrogen bond (C–H···O) to construct a supramolecular structure (Fig. 3c).

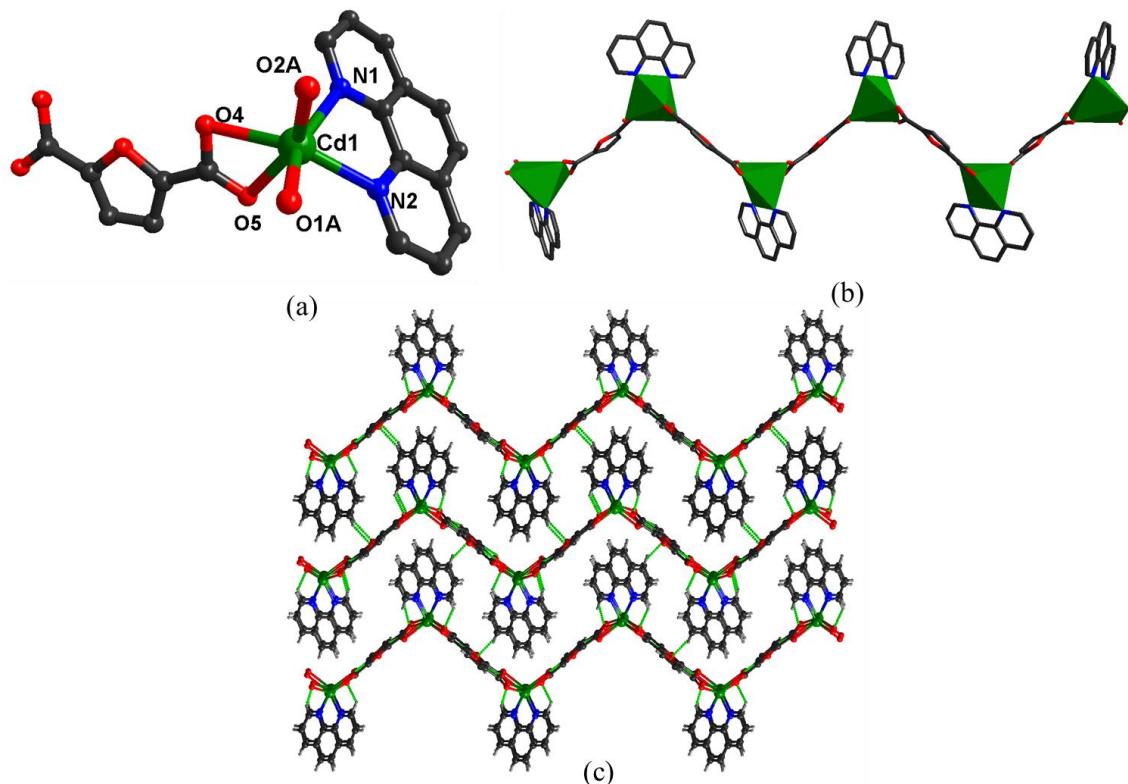


Fig. 3. (a) Asymmetric unit of 3. (b) 1D zig-zag chain in 3. (c) 3D supramolecular structure of 3

3.3 Powder X-ray diffraction of 1 and 2

The experimental PXRD patterns of **1**~**3** match well with their simulated ones, demonstrating that the samples were pure phase (Fig. 4). The difference in reflection intensities among the simulated and experimental patterns may be attributed to the preferred orientation of the crystalline powder samples.

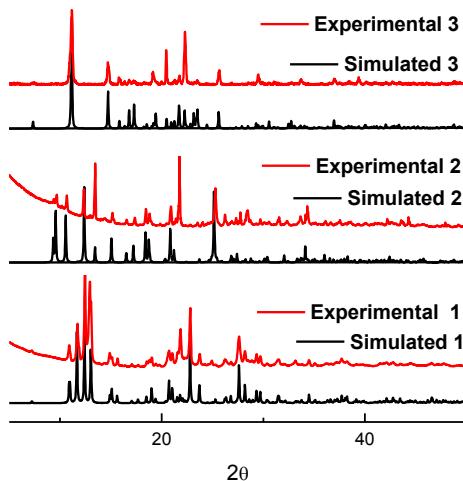


Fig. 4. Simulated PXRD patterns and the experimental PXRD patterns of **1~3**

3.4 Thermal analysis

Thermogravimetric analyses were carried out on complexes **1~3** to investigate their degradation behavior in a temperature range of 30~700 °C at a heating rate of 10 °C/min under nitrogen atmosphere, as shown in Fig. 5. For complex **1**, the first weight loss of 8.21% (calcd: 8.26%) in the range of 60~106 °C is attributed to the removal of a lattice and a coordination water molecules per unit cell. Then, the weight of complex **1** is stable until 310 °C. Subsequently, the organic framework of complex **1** dramatically collapses due to the decomposition of organic ligands, and the final residues are ZnO (obs.: 18.60%, calcd.: 18.69%). The thermal stabilities of complexes **2** and **3** are 210 and 310 °C, respectively. The final residues are CdO (obs.: 18.58%, calcd.: 18.64% for **1**, and obs.: 28.81%, calcd.: 28.75% for **2**).

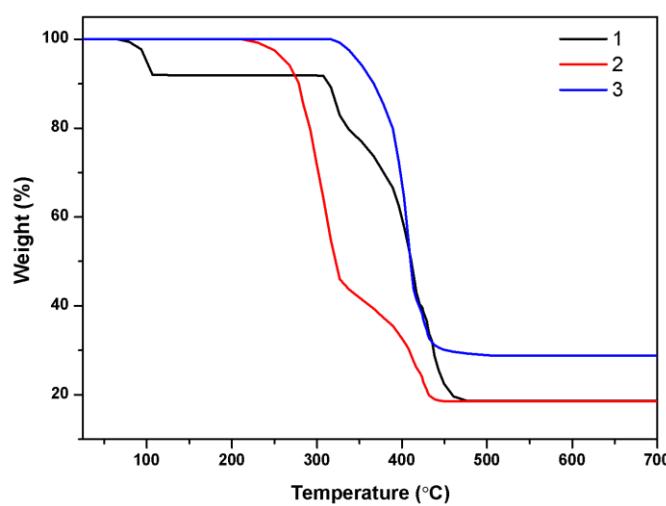


Fig. 5. TGA curves for complexes **1~3**

3.5 Photoluminescent properties

As a series of d^{10} metal-organic coordination polymers, the emission spectra of complexes **1~3** and corresponding organic ligands have been recorded in the solid state at room temperature. As shown in Fig. 6, the emission bands are 377 nm ($\lambda_{\text{ex}} = 312$ nm) for H₂FDA, and 416, 439 and 465 nm ($\lambda_{\text{ex}} = 380$ nm) for phen, respectively. The emission spectra of **1**, **2** and **3** were observed with a maximum emission peak at 390 nm ($\lambda_{\text{ex}} = 359$ nm), 386 nm ($\lambda_{\text{ex}} = 346$ nm), 393 nm ($\lambda_{\text{ex}} = 353$ nm), respectively. Compared with the free ligand, the photoluminescence intensity of **1** is enhanced, but the photoluminescence intensities of **2** and **3** are reduced. The enhanced photoluminescence intensity may originate from the unique structure of **1** with increasing the rigidity of the structure and reducing the loss of energy by radiation-less decay of vibrational motions^[12]. And there are abundant hydrogen bonds in **1** compared with other complexes, which may be contributed to the photoluminescence. Thus complex **1** may potentially be used in the development of photoluminescent materials.

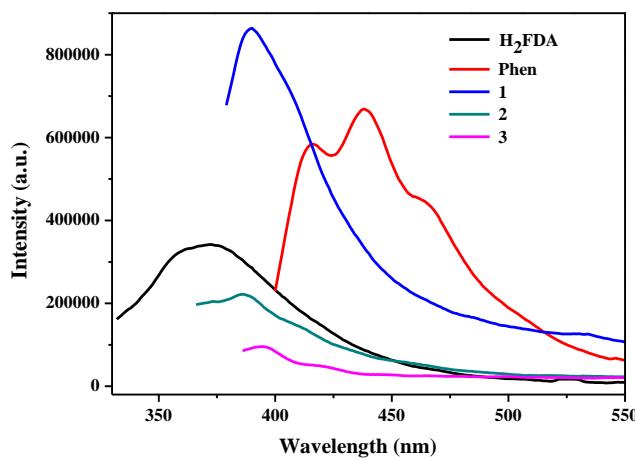


Fig. 6. Emission spectra of **1~3** and the corresponding organic ligands

4 CONCLUSION

In summary, three new coordination polymers showing diverse structures have been synthesized under solvothermal conditions by reacting H₂FDA and N-containing auxiliary ligand phen with different metal ions. Due to the chelation of phen, three coordination polymers have low dimensions, namely 1D for **1**, 0D for **2**, and 1D for **3**. H₂FDA is partial deprotonation in **2**, which is a rare phenomenon among other coordination polymers based on H₂FDA. Furthermore, luminescent properties of three complexes are also investigated.

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Crystal Structures and Luminescent Properties of Three Coordination Polymers Based on 2,5-Furandicarboxylic Acid Ligand and 1,10-Phenanthroline

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Three new coordination polymers of $[\text{Zn}(\text{FDA})(\text{phen})(\text{H}_2\text{O}) \text{H}_2\text{O}]_n$ (**1**), $[\text{Cd}(\text{HFDA})(\text{phen})_2(\text{NO}_3)]$ (**2**) and $[\text{Cd}(\text{FDA})(\text{phen})]_n$ (**3**) (H_2FDA = 2,5-furandicarboxylic acid, phen = 1,10-phenanthroline) have been synthesized by solvothermal method. For **1**, the neighboring Zn^{2+} ions are bridged by FDA^{2-} as linkers to form one-dimensional (1D) chains, and phen ligands serve as the terminal ligands. For **2**, the H_2FDA ligand is partial deprotonation, which is a rare phenomenon among other coordination polymers based on H_2FDA . Under the synergetic effect of phen ligands and the partial deprotonation of H_2FDA , the structure of **2** is discrete. For **3**, the Cd^{2+} ions are linked by two carboxylates of FDA^{2-} ligand to give rise to 1D zig-zag chains, and phen ligands chelate the Cd^{2+} ions like **1**.

